12-28-01

FORM PTO-1390 (REV. 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 427.051

US APPLICATION NO. (If known, see 37 CFR 1.5): 10/019167

IC10 Rec'd PCT/PTO 20 DEC 2001

INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/01753	6/23/00	6/25/99

TITLE OF INVENTION: POLYMERISATION CATALYSTS

APPLICANT(S) FOR DO/EO/US: Hanh Nguyen Ngoc, et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This is an express request to begin national examination procedures (35 U S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [ ] The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. [X] A copy of the International Application as filed (35 U.S C. 371(c)(2))
   a. [X] is attached hereto (required only if not communicated by the International Bureau).
   b. [ ] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] An English language translation of the International Application as filed (35 U.S C. 371(c)(2))
   a. [X] is attached hereto.
   b. [ ] has been previously submitted under 35 U S.C. 154(d)(4)
7. [ ] Amendments to the claims of the International Aplication under PCT Article 19 (35 U S C. 371(c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau)
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made, however, the time limit for making such amendments has NOT expired
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U S C 371 (c)(3))
9. [XX] An oath or declaration of the inventor(s) (35 U S C. 371(c)(4))
10. [ ] An English lanugage translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U S C 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. [XX] An Information Disclosure Statement under 37 CFR 1.97 and 1.98
12. [XX] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3 31 is included.
13. [XX] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter 2 and 35 U.S.C. 1 821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C 154(d)(4).
20. [ ] Other items or information: copy of PCT/IB/332
    PTO-2038

U.S. APPLICATION NO (if known, see 37 CFR 1.5) 10/019167 | INTERNATIONAL APPLICATION NO | ATTORNEY'S DOCKET NUMBER 1001.1362101

531 Rec'd PCT/PTO 20 DEC 2001

21. ☐ The following fees are submitted	CALCULATIONS PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 1040.00
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	- 20 =		x **$18.00**	$
Independent claims	- 3 =		x **$80.00**	$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$270.00**	$
TOTAL OF ABOVE CALCULATIONS =				$
☐ Applicant claims small entity status. See 37 CFR 1.27 The fees indicated above are reduced by 1/2.			+	$
SUBTOTAL =				$ 1040.00
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$
TOTAL NATIONAL FEE =				$ 1040.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00
TOTAL FEES ENCLOSED =				$ 1080.00
			Amount to be refunded:	$
			charged:	$

a. ☐ A check in the amount of $ _____ to cover the above fees is enclosed

b. ☐ Please charge my Deposit Account No. _____ in the amount of $ _____ to cover the above fees. A duplicate copy of this sheet is enclosed

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-2275. A duplicate copy of this sheet is enclosed

d. ☒ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

PTO-2038 in the amount of $1080.00

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Charles A. Muserlian
Bierman, Muserlian and L
600 Third Avenue
New York, NY 10016

20311
PATENT TRADEMARK OFFICE

SIGNATURE

Charles A. Muserlian
NAME

19,683
REGISTRATION NUMBER

Our ref: 427.051

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: NGUYEN NGOC, et al		
Serial No. :		International Appln. PCT/FR00/01753
Filed :	Concurrently herewith	Filed: June 23, 2000
For :	POLYMERIZATION CATALYSTS	

600 Third Avenue
New York, N.Y. 10016

Dated : December 20, 2001

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, D.C. 20231

S i r:

Please amend this application as follows:

IN THE SPECIFICATION:

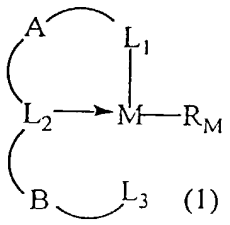
Page 1, before line 1, insert

--This application is a 371 of PCT FR00/01753, filed June 23, 2000. --

IN THE CLAIMS

Claims 1 to 8 and 12 to 14 are amended.

--1. (Amended) A compound of the formula



(I)

wherein

M is an element of group 12 of the Periodic Table;

R_M is selected from the group consisting of hydrogen, halogen, alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino and (cycloalkyl)arylamino;

A and B are independently selected from the group consisting of carbon chain of 2 to 4 carbon atoms, optionally substituted by at least one member of the group consisting of substituted or non-substituted alkyl, cycloalkyl, and aryl, the substituent is selected from the group consisting of halogen, alkyl, nitro and cyano;

L_1 and L_2 are independently $-E_{15}(R15)-$ in which E_{15} is an element of group 15 of the Periodic Table and R_{15} is selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl and aryl, in which said substitutent is selected from the group consisting of halogen, alkyl, nitro and cyano or $-E_{14}RR'R"$ in which E_{14} is an element of group 14 of the Periodic Table and R, R' and R" are independently selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio and arylthio, in which the substituents are at least one member of the group consisting of halogen, alkyl, nitro and cyano; or $-SO_2Q$ in which Q is selected from the group consisting of halogen, alkyl, haloalkyl and aryl optionally substituted by at least one

substituent selected from the group consisting of alkyl, haloalkyl and halogen;

L_3 is $-E'_{15}(R'_{15})(R"_{15})$ or $-E_{16}(R_{16})$ in which

E'_{15} is an element of group 15 of the Periodic Table and

E_{16} is an element of group 16 of the Periodic Table and

R'_{15}, and $R"_{15}$ and R_{16} are, independently, selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl and aryl, in which the substituents are at least one member of the group consisting of halogen, alkyl, nitro and cyano or $-E'_{14}TT'T"$ in which E'_{14} is an element of group 14 of the Periodic Table and T, T' and T" are independently selected from the group consisting of hydrogen, substituted or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio and arylthio, in which said substitutents are at least one member of the group consisting of halogen, alkyl, nitro and cyano; or $-SO_2Q'$ in which Q' is selected from the group consisting of halogen, alkyl, haloalkyl and aryl optionally substituted by at least one member of the group consisting of alkyl, haloalkyl and halogen. --

--2. (Amended) A compound of claim 1, in the form of a monomer or a dimer. --

--3. (Amended) A compound of claim 1 wherein

R_M is alkyl;

A and B are, independently, a carbon chain of 2 to 4 carbon atoms;

L_1 and L_2 are, independently, $-E_{15}(R_{15})-$ in which E_{15} is nitrogen or phosphorus and R_{15} is hydrogen or $-E_{14}RR'R"$ in which E_{14} is carbon or silicon and R, R' and R" are, independently, hydrogen or alkyl;

L_3 is $-E'_{15}(R'_{15})(R"_{15})$ in which E'_{15} is nitrogen or phosphorus, and R'_{15} and $R"_{15}$ are, independently, hydrogen or $-E'_{14}TT'T"$ in which E'_{14} is carbon or silicon atom and T, T' and T" are independently, hydrogen or alkyl.

--4. (Amended) A compound of claim 1 wherein M is zinc. --

--5. (Amended) A compound of claim 1 wherein

R_M is methyl;

A and B are, independently, a carbon chain of 2 carbon atoms;

L_1 and L_2 are, independently, $-E_{15}(R_{15})-$ in which E_{15} is nitrogen and R_{15} is selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl and $-E_{14}RR'R"$ in which E_{14} is silicon and R, R' and R" are, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl and isopropyl;

L_3 is $-E'_{15}(R'_{15})(R"_{15})$ in which E'_{15} is nitrogen, and R'_{15} and $R"_{15}$ are, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl and $-E'_{14}TT'T"$ in which E'_{14} is silicon and T, T'and T" are, independently, selected from the group consisting of hydrogen, methyl, ethyl, propyl, and isopropyl. --

--6. (Amended) A compound of claim 1 which is

- $[Me_3SiN(H)CH_2CH_2N(Me)CH_2CH_2NSiMe_3]ZnMe$; or
- $[Me_3SiN(H)CH_2CH_2N(H)CH_2CH_2NSiMe_3]ZnMe$. --

--7. (Amended) A compound of claim 6 in dimer form. --

--8. (Amended) A process for the preparation of a compound of claim 1, comprising reacting a compound of the formula

$$(L_1\text{-}A\text{-}L_2\text{-}B\text{-}L_3)^-,\ Y^+ \qquad (I)$$

wherein L_1, A, L_2, B and L_3 are defined as claim 1 and Y is hydrogen or metal or a metallic with a compound of the formula

$$MR_MZ \qquad (II)$$

in which M and R_M are defined as in claim 1 and Z is a parting group, to obtain a compound of claim 1.

--12. (Amended) A process for the preparation of block or random copolymers, or polymers which comprises contacting at least one monomer, a chain initiator and/or a regulator, a polymerization catalyst and optionally a polymerization solvent, at a temperature between ambient temperature and 250°C, for a few minutes to 300 hours, wherein the chain initiator and/or the regulator and the polymerization catalyst are a compound of claim 1. --

--13. (Amended) The process of claim 12, wherein the monomer is selected from the group consisting of epoxides, and cyclic esters. --

--14. (Amended) A polymer or copolymer prepared by the process of claim 12. --

Cancel claims 9 to 11 and add the following claims.

--15. In a process for the polymerization or copolymerization of heterocycles, the improvement comprising using as the polymerization catalyst a compound of claim 1. --

--16. The process of claim 15 wherein the heterocycle is propylene oxide. --

--17. In a process for the polymerization or copolymerization of cyclic esters, the improvement comprising using as the polyermization catalyst a compound of claim 1. --

--18. The process of claim 17 wherein the cyclic ester is that of lactic acid and/or glycolic acid. --

REMARKS

The amendments is submitted to insert reference to the PCT application, to remove multiple dependency from the claims and to comform the claims to the American practice.

Respectfully submitted,

Bierman, Muserlian & Lucas

By: _____

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Encl: Marked-up copy of Amended Claims

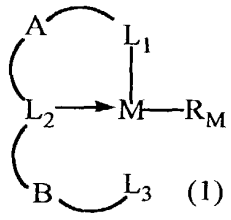
POLYMERISATION CATALYSTS

The present invention relates to new compounds having an element of group 12 and having a tridentate ligand, a process for their preparation and their use in particular as polymerization catalysts.

The use of derivatives having an element of group 12 but having porphyrin type ligands (Inoue, Acc. Chem. Res., (1996) 29, 39) as catalysts for the polymerization of heterocycles is already known.

However, it has been shown that each type of catalyst used for the polymerizations or copolymerizations, produces different polymers or copolymers respectively (Jedlinski et al., Macromolecules, (1990) 191, 2287; Munson et al., Macromolecules, (1996) 29, 8844; Montaudo et al., Macromolecules, (1996) 29, 6461). The problem is therefore to find new catalytic systems in order to obtain new polymers or copolymers, and more particularly block copolymers. The use of catalytic systems allows control of the chain formation of monomers leading to specific copolymers having the appropriate properties. This is particularly useful for biocompatible copolymers, the biodegradation of which is influenced by this chain formation.

Therefore a subject of the invention is the products of general formula 1



(1)

in which

M represents an element of group 12;

R_M represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino or (cycloalkyl)arylamino radical;

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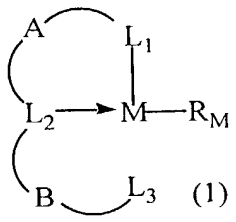
CLAIMS

1. Compounds of general formula



(1)

in which

M represents an element of group 12,

R_M represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino or (cycloalkyl)arylamino radical;

A and B represent, independently, a carbon chain of 2 to 4 carbon atoms, optionally substituted by one or more of the following substituted or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, an alkyl, nitro or cyano radical;

L_1 and L_2 represent, independently, a group of formula $-E_{15}(R_{15})-$ in which

E_{15} is an element of group 15 and

R_{15} represents the hydrogen atom; one of the following substituted or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, an alkyl, nitro or cyano radical; a radical of formula $-E_{14}RR'R''$ in which E_{14} is an element of group 14 and R, R' and R'' represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or arylthio radicals, in which said substituents is a halogen atom, the alkyl, nitro or cyano radical; or a radical of formula $-SO_2Q$ in which Q represents a halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by

one ~~or more~~ substituents ~~chosen~~ from the alkyl, haloalkyl and halogen ~~radicals~~;

L_3 ~~indifferently represents a group of formula~~ $-E'_{15}(R'_{15})(R''_{15})$ or $-E_{16}(R_{16})$ in which

E'_{15} is an element of group 15 and

E_{16} is an element of group 16 and

R'_{15}, R''_{15} and R_{16} ~~represent,~~ independently, ~~the~~ hydrogen ~~atom; one of the following~~ substituted ~~(by one or more identical or different substituents)~~ or non-substituted alkyl, cycloalkyl ~~or~~ aryl ~~radicals~~, in which ~~said~~ substituents is ~~a~~ halogen ~~atom~~, ~~the~~ alkyl, nitro ~~and~~ cyano ~~radical~~; ~~a radical of formula~~ $-E'_{14}TT'T''$ in which E'_{14} is an element of group 14 and T, T' and T'' ~~represent~~, independently, ~~the~~ hydrogen ~~atom or one of the following~~ substituted ~~(by one or more identical or different substituents)~~ or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio ~~and~~ arylthio ~~radicals~~, in which said substituents is a halogen ~~atom~~, ~~the~~ alkyl, nitro ~~and~~ cyano ~~radical~~; or ~~a radical of formula~~ $-SO_2Q'$ in which Q' ~~represents a~~ halogen ~~atom~~, an alkyl, haloalkyl ~~or~~ aryl ~~radical~~ optionally substituted by ~~one or more substituents chosen from the~~ alkyl, haloalkyl and halogen ~~radicals.~~

2. ~~Compounds of formula I as defined in~~ claim 1, ~~characterised in that they are presented~~ in the form of a monomer or a dimer.

3. ~~Compounds of general formula I as defined in one of~~ claims 1 ~~to 2, characterised in that~~

R_M ~~represents an~~ alkyl ~~group~~;

A and B ~~represent~~, independently, a carbon chain of 2 to 4 carbon atoms;

L_1 and L_2 ~~represent~~, independently, ~~a radical of formula~~ $-E_{15}(R_{15})-$ in which E_{15} is ~~a~~ nitrogen or phosphorus ~~atom~~ and R_{15} ~~represents a~~ hydrogen ~~atom~~ or ~~a radical of formula~~ $-E_{14}RR'R''$ in which E_{14} ~~represents a~~ carbon or silicon ~~atom~~ and R, R' and R'' ~~represent~~, independently, ~~the~~ hydrogen ~~atom~~ or ~~an~~ alkyl ~~radical~~;

L_1 ~~represents a radical of formula~~ $-E'_{15}(R'_{15})(R''_{15})$ in which E'_{15} is ~~a~~ nitrogen or phosphorus ~~atom~~, and R'_{15} and R''_{15} ~~represent~~, independently, ~~a~~ hydrogen ~~atom~~ or ~~a radical of formula~~ $-E'_{14}TT'T''$ in which E'_{14} ~~represents~~ a carbon or silicon atom and T, T' and T'' ~~represent~~, independently, ~~the~~ hydrogen ~~atom~~ or ~~an~~ alkyl ~~radical~~.

4. ~~Compounds of general formula I as defined in one of~~ claims 1 ~~to 3, characterized in that~~ M ~~represents a~~ zinc ~~atom~~.

5. Compounds of general formula I as defined in one of claims 1 to 4, characterized in that

R_M represents a methyl radical;

A and B represent, independently, a carbon chain of 2 carbon atoms;

L_1 and L_2 represent, independently, a radical of formula $-E_{15}(R_{15})-$ in which E_{15} is a nitrogen atom and R_{15} represents a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula $-E_{14}RR'R''$ in which E_{14} represents a silicon atom and R, R' and R'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical;

L_3 represents a radical of formula $-E'_{15}(R'_{15})(R''_{15})$ in which E'_{15} is a nitrogen atom, and R'_{15} and R''_{15} represent, independently, a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula $-E'_{14}TT'T''$ in which E'_{14} represents a silicon atom and T, T' and T'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical.

6. Compounds of general formula I as defined in one of claims 1 to 4 and corresponding to the following formulae:

- $[Me_3SiN(H)CH_2CH_2N(Me)CH_2CH_2NSiMe_3]ZnMe$;
- $[Me_3SiN(H)CH_2CH_2N(H)CH_2CH_2NSiMe_3]ZnMe$.

7. Compounds of formula I as defined in claim 6, characterised in that they are presented in dimer form.

8. Process for the preparation of the products of general formula I as defined in claim 1, characterized in that a product of formula I

$$(L_1\text{-}A\text{-}L_2\text{-}B\text{-}L_3)^-, Y^+ \quad (I)$$

in which L_1, A, L_2, B and L_3 have the meanings indicated in claim 1 and Y represents the hydrogen atom, a metal or a metallic group, is reacted with a product of formula II

$$MR_MZ \quad (II)$$

in which M and R_M have the meanings indicated in claim 1 and Z represents a parting group, in order to obtain a product of formula I.

9. Use of the products of formula I as defined in any one of claims 1 to 7, as polymerization or copolymerization catalyst.

10. Use according to claim 9 for the polymerization or copolymerization of heterocycles, in particular epoxides such as propylene oxide.

11. Use according to claim 9, for the polymerization or copolymerization of cyclic esters, in particular the polymer cyclic esters of lactic and/or glycolic acid.

12. A process for the preparation of block or random copolymers, or polymers which ~~consist of bringing into~~ comprises contact with at least one ~~or more~~ monomers, a chain initiator and/or a regulator, a polymerization catalyst and optionally a polymerization solvent, at a temperature ~~comprised~~ between ambient temperature and 250° C, for ~~a duration comprised between~~ a few minutes ~~and~~ to 300 hours, ~~said process characterized in that~~ wherein the chain initiator and/or the regulator and the polymerization catalyst are ~~represented by the same~~ are a compound ~~which is chosen from the compounds according to claims 1 to 7.~~ of claim 1

13. The process ~~according to~~ of claim 12, ~~characterized in that~~ wherein the monomer is ~~chosen~~ selected from the group consisting of epoxides, ~~and in particular propylene oxide, or the~~ cyclic esters, ~~and in particular the polymer cyclic esters of lactic and/or glycolic acid.~~

14. A polymers or copolymers ~~which can be obtained by carrying out a~~ prepared by the process ~~according to one of~~ of claims 12 ~~or 13.~~

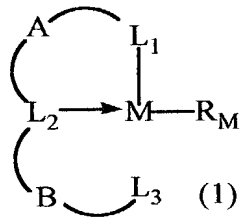
POLYMERISATION CATALYSTS

The present invention relates to new compounds having an element of group 12 and having a tridentate ligand, a process for their preparation and their use in particular as polymerization catalysts.

The use of derivatives having an element of group 12 but having porphyrin type ligands (Inoue, Acc. Chem. Res., (1996) 29, 39) as catalysts for the polymerization of heterocycles is already known.

However, it has been shown that each type of catalyst used for the polymerizations or copolymerizations, produces different polymers or copolymers respectively (Jedlinski et al., Macromolecules, (1990) 191, 2287; Munson et al., Macromolecules, (1996) 29, 8844; Montaudo et al., Macromolecules, (1996) 29, 6461). The problem is therefore to find new catalytic systems in order to obtain new polymers or copolymers, and more particularly block copolymers. The use of catalytic systems allows control of the chain formation of monomers leading to specific copolymers having the appropriate properties. This is particularly useful for biocompatible copolymers, the biodegradation of which is influenced by this chain formation.

Therefore a subject of the invention is the products of general formula 1



(1)

in which

M represents an element of group 12;

R_M represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino or (cycloalkyl)arylamino radical;

A and B represent, independently, a carbon chain of 2 to 4 carbon atoms, optionally substituted by one or more of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical;

L_1 and L_2 represent, independently, a group of formula $-E_{15}(R_{15})$ - in which
E_{15} is an element of group 15 and
R_{15} represents the hydrogen atom; one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; a radical of formula $-E_{14}RR'R''$ in which E_{14} is an element of group 14 and R, R' and R" represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or arylthio radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; or a radical of formula $-SO_2Q$ in which Q represents a halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by one or more substituents chosen from the alkyl, haloalkyl and halogen radicals.

L_3 indifferently represents a group of formula $-E'_{15}(R'_{15})(R''_{15})$ or $-E_{16}(R_{16})$ in which
E'_{15} is an element of group 15 and
E_{16} is an element of group 16 and
R'_{15}, R''_{15} and R_{16} represent, independently, the hydrogen atom; one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; a radical of formula $-E'_{14}TT'T''$ in which E'_{14} is an element of group 14 and T, T' and T" represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or arylthio radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; or a radical of formula $-SO_2Q'$ in which Q' represents a halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by one or more substituents chosen from the alkyl, haloalkyl and halogen radicals.

In the definitions indicated above, the expression halogen represents a fluorine, chlorine, bromine or iodine atom, preferably chlorine. The expression alkyl preferably represents a

linear or branched alkyl radical having 1 to 6 carbon atoms and in particular an alkyl radical having 1 to 4 carbon atoms such as the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl and tert-butyl radicals.

The term haloalkyl preferably designates radicals in which the alkyl radical is as defined above and is substituted by one or more halogen atoms as defined above such as, for example, bromoethyl, trifluoromethyl, trifluoroethyl or also pentafluoroethyl. The alkoxy radicals can correspond to radicals in which the alkyl radical is as defined above. The methoxy, ethoxy, isopropyloxy or tert-butyloxy radicals are preferred. The alkylthio radicals preferably represent radicals in which the alkyl radical is as defined above such as, for example, methylthio or ethylthio. The alkylamino and dialkylamino radicals preferably represent the radicals in which the alkyl radical is as defined above such as, for example, methylamino or dimethylamino.

The cycloalkyl radicals are chosen from saturated or unsaturated monocyclic cycloalkyls. The saturated monocyclic cycloalkyl radicals can be chosen from the radicals having 3 to 7 carbon atoms such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl radicals. The unsaturated cycloalkyl radicals can be chosen from cyclobutene, cyclopentene, cyclohexene, cyclopentadiene and cyclohexadiene radicals. The cycloalkoxy radicals can correspond to radicals in which the cycloalkyl radical is as defined above. The cyclopropyloxy, cyclopentyloxy or cyclohexyloxy radicals are preferred. The cycloalkylthio radicals can correspond to radicals in which the cycloalkyl radical is as defined above such as for example cyclohexylthio. The cycloalkylamino and di(cycloalkyl)amino radicals can correspond to radicals in which the cycloalkyl radical is as defined above such as for example cyclohexylamino and di(cyclohexyl)amino.

The aryl radicals can be of mono or polycyclic type. The monocyclic aryl radicals can be chosen from the phenyl radicals optionally substituted by one or more alkyl radicals, such as tolyl, xylyl, mesityl and cumenyl. The polycyclic aryl radicals can be chosen from the naphthyl, anthryl and phenanthryl radicals. The aryloxy radicals can correspond to radicals in which the aryl radical is as defined above. The phenoxy, 2,4,6-tritertiobutylphenoxy, tolyloxy or mesityloxy radicals are preferred. The arylthio radicals preferably designate the radicals in which the aryl radical is as defined above such as for example in phenylthio radicals. The arylamino and diarylamino radicals preferably designate radicals in which the aryl radical is as defined above such as, for example, phenylamino or diphenylamino radicals.

The alkyl (cycloalkyl)amino radicals can correspond to radicals in which the alkyl and cycloalkyl radicals are as defined above such as, for example methyl(cyclohexyl)amino. The alkyl arylamino radicals preferably designate radicals in which the alkyl and aryl

radicals are as defined above such as, for example methylphenylamino. The (cycloalkyl)arylamino radicals can correspond to the radicals in which the cycloalkyl and aryl radicals are as defined above such as, for example (cyclohexyl)phenylamino.

The compounds of formula 1 can be presented in the form of a monomer or of a dimer and more particularly the compounds of formula 1 in which M represents a zinc atom generally presented in dimer form.

A more particular subject of the invention is the products of general formula 1 as defined above, characterized in that
R_M represents an alkyl radical;
A and B represent, independently, a carbon chain with 2 to 4 carbon atoms;
L_1 and L_2 represent, independently, a radical of formula $-E_{15}(R_{15})-$ in which E_{15} is a nitrogen or phosphorus atom and R_{15} represents a hydrogen atom or a radical of formula $-E_{14}RR'R''$ in which E_{14} represents a carbon or silicon atom and R, R' and R" represent, independently, the hydrogen atom or an alkyl radical;
L_3 represents a radical of formula $-E'_{15}(R'_{15})(R''_{15})$ in which E'_{15} is a nitrogen or phosphorus atom, and R'_{15} and R''_{15} represent, independently, a hydrogen atom or a radical of formula $-E'_{14}TT'T''$ in which E'_{14} represents a carbon or silicon atom and T, T' and T" represent, independently, the hydrogen atom or an alkyl radical.

Preferably, M represents a zinc atom. Preferably also, R_M represents a methyl radical; A and B represent, independently, a carbon chain with 2 carbon atoms; L_1 and L_2 represent, independently, a radical of formula $-E_{15}(R_{15})-$ in which E_{15} is a nitrogen atom and R_{15} represents a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula $-E_{14}RR'R''$ in which E_{14} represents a silicon atom and R, R' and R" represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical; L_3 represents a radical of formula $-E'_{15}(R'_{15})(R''_{15})$ in which E'_{15} is a nitrogen atom, and R'_{15} and R''_{15} represent, independently, a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula $-E'_{14}TT'T''$ in which E'_{14} represents a silicon atom and T, T' and T" represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical.

More particularly, a subject of the invention is the products described hereafter in the examples, in particular the products corresponding to the following formulae:

- $[Me_3SiN(H)CH_2CH_2N(Me)CH_2CH_2NSiMe_3]ZnMe$;
- $[Me_3SiN(H)CH_2CH_2N(H)CH_2CH_2NSiMe_3]ZnMe$.

A subject of the invention is also a process for the preparation of the products of general formula 1 as defined above, characterized in that a product of formula I

$(L_1\text{-}A\text{-}L_2\text{-}B\text{-}L_3)^-, Y^+$ (I)

in which L_1, A, L_2, B and L_3 have the meanings indicated above and Y represents the hydrogen atom, a metal or a metallic group, is reacted with a product of formula II

MR_MZ (II)

in which M and R_M have the meanings indicated above and Z represents a parting group, in order to obtain a product of formula 1 as defined above.

The reaction of a compound of general formula I with a compound of general formula II in order to obtain a compound of general formula 1, can be carried out under an inert atmosphere such as under a freon or argon atmosphere, in an aprotic solvent, at a temperature comprised between -90 and +50° C. The compounds I thus obtained are purified by standard purification methods.

As aprotic solvent, aromatic hydrocarbons such as benzene, toluene; aliphatic hydrocarbons such as pentane, heptane, hexane, cyclohexane; ethers such as diethylether, dioxane, tetrahydrofuran, ethyltertiobutyl ether can be used.

In the Compounds I, Y represents the hydrogen atom, a metal or a metallic group. The metallic group can be a compound of formula $R'''M_1$ or R'''_3M_2 in which R''' represents a halogen atom, or indifferently, an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy or aryloxy radical as previously defined, M_1 is a zinc or mercury atom or an alkaline-earth such as magnesium and M_2 a tin or lead atom; preferably, the metallic group is chosen from the MgBr, ZnMe, $SnMe_3$, $SnBu_3$ or $PbMe_3$ groups. The metal can be an alkali metal chosen from lithium, sodium or potassium.

In the compounds II, Z represents a parting group such as a halogen atom, an alkyl, cycloalkyl, alkoxy, aryl, aryloxy, amino, alkylamino or dialkylamino group as previously defined, or also a methanesulphonyloxy, a benzenesulphonyloxy, p-toluenesulphonyloxy group.

The starting products of formula I are known products or can be prepared from known products. For their synthesis, the following references can be mentioned: Cloke et al., J. Chem. Soc., Dalton Trans. (1995) 25; Wilkinson and Stone, Comprehensive Organometallic Chemistry (1982) vol. 1, 557.

The products of formula II are commercially available or can be manufactured by methods known to a person skilled in the art.

A subject of the invention is also the use of the products of formula 1 as defined above, as catalysts for carrying out (co)polymerization, that is to say of polymerization or copolymerization. Whilst carrying out (co)polymerization, the compounds according to the invention also play the role of chain initiator and/or of regulator.

The compounds of formula 1 are particularly useful for carrying out the polymerization of heterocycles. The heterocycles can contain one or more heteroatoms of groups 15 and/or 16, and have a size ranging from three to eight members. As an example of heterocycles corresponding to the previous formulation, epoxides, thioepoxides, cyclic esters or thioesters such as lactones, lactames and anhydrides can be mentioned.

The compounds of formula 1 are also particularly useful for carrying out the (co)polymerization of cyclic esters. As an example of cyclic esters, the polymer cyclic esters of lactic and/or glycolic acid can be mentioned. Random or block copolymers can be obtained depending on whether the monomers are introduced together at the start of the reaction, or sequentially during the course of the reaction.

A subject of the invention is also a process for the preparation of random or block copolymers, or polymers which consists of bringing into contact one or more monomers, a chain initiator and/or a regulator, a polymerization catalyst and optionally a polymerization solvent, said process characterized in that the chain initiator and/or chain regulator and the polymerization catalyst are represented by the same compound which is chosen from the compounds of formula (1) as defined above.

The (co)polymerization can be carried out either in solution or in supercooling. When the (co)polymerization is carried out in solution, the reaction solvent can be the (or one of the) substrate(s) used in the catalytic reaction. Solvents which do not interfere with the catalytic reaction itself, are also suitable. As an example of such solvents, saturated or aromatic hydrocarbons, ethers, aliphatic or aromatic halides can be mentioned.

The reactions are carried out at temperatures comprised between ambient temperature and approximately 250° C; the temperature range comprised between 40 and 200° C is most advantageous. The durations of the reactions are comprised between a few minutes and 300 hours, and preferably between 5 minutes and 72 hours.

This (co)polymerization process is particularly suitable for obtaining (co)polymers of cyclic esters, in particular the polymer cyclic esters of lactic and/or glycolic acid. The products obtained such as the biodegradable glycolic lactic copolymers, are advantageously used as a support in sustained release therapeutic compositions. The process is also particularly well suited to the polymerization of epoxides, in particular propylene oxide.

The polymers obtained are compounds which can be used for the synthesis of organic liquid crystals or also as semi-permeable membranes.

The invention also relates to the polymers or copolymers which can be obtained by carrying out a process as described above.

The following examples are presented to illustrate the above procedures and should in no way be considered as limiting the scope of the invention.

Example 1: $[Me_3SiN(H)CH_2CH_2N(H)CH_2CH_2NSiMe_3]ZnMe$ (in dimer form)

4.3 g (17.7 mmol) of $[(Me_3SiN(H)CH_2CH_2)_2NH]$ and 30 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is cooled down to -78 C, then 8.8 ml (17.7 mmol) of a 2M solution of $ZnMe_2$ in toluene is introduced. The reaction mixture is brought to ambient temperature then left under agitation for 18 hours at ambient temperature. After evaporating the solvent, an orange oil is obtained. The desired compound is isolated in the form of colourless crystals by crystallization at -20 C from pentane (5 ml) (yield 50 %). This compound is characterized by multinuclear magnetic resonance spectroscopy and X-ray diffraction (Figure 1 and Table 1 below).

Example 2: $[Me_3SiN(H)CH_2CH_2N(Me)CH_2CH_2NSiMe_3]ZnMe$ (in dimer form)

1.1 g (4.2 mmol) of $[(Me_3SiN(H)CH_2CH_2)_2NMe]$ and 20 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is cooled down to -78 C, then 2.1 ml (4.2 mmol) of a 2M solution of $ZnMe_2$ in toluene is introduced. The reaction mixture is brought to ambient temperature then left under agitation for 3 hours at ambient temperature. After evaporating the solvent, an orange oil is obtained. The desired compound is isolated in the form of white crystals by crystallization at -20° C from pentane (5 ml) (yield 50 %). This compound is characterized by multinuclear magnetic resonance spectroscopy.

Example 3: preparation of a poly(D,L-lactide)

0.045 g (0.14 mmol) of $[Me_3SiN(H)CH_2CH_2$-$N(H)CH_2CH_2NSiMe_3]ZnMe$ and 100 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is brought to 80°C. 6.24 g (43.2 mmol) of D,L-lactide is then added. The reaction mixture is left under agitation at 80 °C for 42 hours. The polymer is characterized by carbon and proton NMR; the conversion of the monomer is 96 %. According to a GPC analysis (Gel Permea Chromatography) using a calibration carried out from polystyrene (PS) standards polystyrene standards of masses

761 to 400000, the sample is comprised of polymers having high masses (Mw = 40400 Dalton).

Example 4: preparation of a block (D,L-lactide / glycolide) copolymer

0.15 g (0.43 mmol) of $[Me_3SiN(H)CH_2CH_2\text{-}N(Me)CH_2CH_2NSiMe_3]ZnMe$, 3.50 g (24 mmol) of D,L-lactide and 80 ml of toluene are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is left under agitation at 85 °C for 18 hours. Proton NMR Analysis of the allows verification that the conversion of the monomer is greater than 94 %. 2.25 g (19.4 mmol) of glycolide is added over a period of 11 days to the previous solution maintained under agitation at 80° C. Analysis of an aliquot by proton NMR shows that a copolymer is formed. The ratio of the signal integrals corresponding to the polylactide part (5.20 ppm) and polyglycolide part (4.85 ppm) is 4/1. According to a GPC analysis, using a calibration carried out from PS standards of masses of 761 to 400000, this copolymer is a mixture of macromolecules having similar masses (Mw/Mn = 1.63; Mw = 2960 Dalton).

Example 5: preparation of a random (D,L-lactide / glycolide) copolymer

0.05 g (0.15 mmol) of $[Me_3SiN(H)CH_2CH_2\text{-}N(Me)CH_2CH_2NSiMe_3]ZnMe$, 6.66 g (45 mmol) of D,L-lactide and 1.53 g (13 mmol) of glycolide are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is heated to 180° C for 2 hours. The polymer is characterized by proton NMR; the conversion of monomers is total. The ratio of the signal integrals corresponding to the polylactide part (5.20 ppm) and the polyglycolide part (4.85 ppm) is 4/1. According to a GPC analysis, using a calibration carried out from PS standards of masses of 761 to 400000, the sample comprises polymers with a polydispersity (Mw/Mn) of 2.27 and molecular weight (Mw) of 16271 Dalton.

Example 6: preparation of a random (D,L-lactide / glycolide) copolymer having a lactide/ glycolide composition close to 70/30

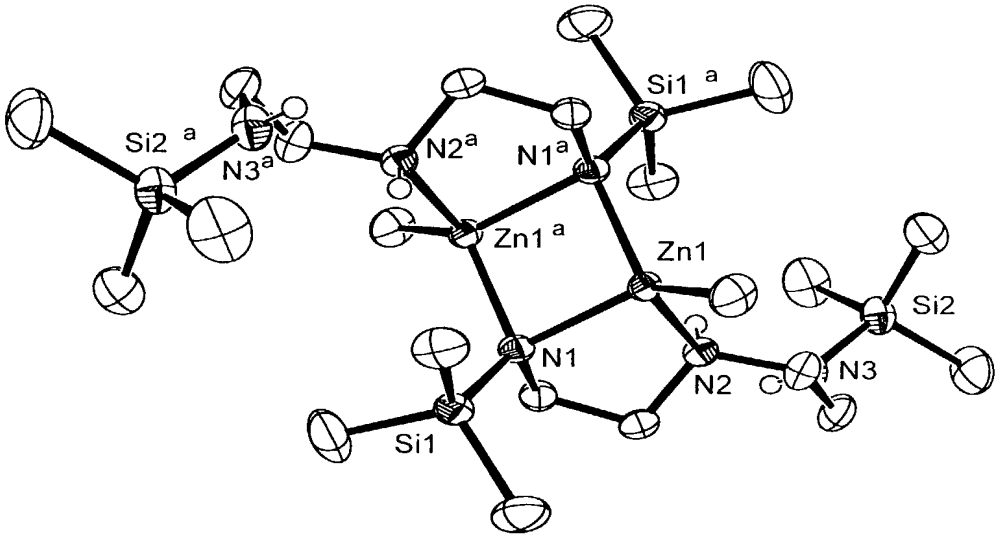
0.024 g (0.073 mmol) of $[Me_3SiN(H)CH_2CH_2\text{-}N(H)CH_2CH_2NSiMe_3]ZnMe$, 1.98 g (13.6 mmol) of D,L-lactide and 0.68 g (5.8 mmol) of glycolide are successively introduced into a Schlenk tube equipped with a magnetic stirrer and purged under argon. The reaction mixture is left under agitation at 180° C for 2 hours. Analysis by proton NMR allows verification that the conversion of the monomers is 98 % lactide and 100% glycolide. The ratio of the signal integrals corresponding to the polylactide part (5.20 ppm) and the polyglycolide part (4.85 ppm) the composition of the copolymer to be evaluated at 65% of lactide and 35% of glycolide. According to a GPC analysis, using a calibration carried out

from PS standards of masses 761 to 400000, this copolymer is a mixture of macromolecules (Mw/Mn = 2.84) of high masses (Mw = 34500 Dalton).

Table 1: **Lengths of the selected bonds (in Angström) and bond angles (in degrees) for the compound of Example 1**

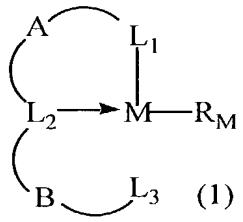
Zn(1)-C(1)	1.989(2) Å	C(5)-C(6)	1.519 (3) Å
Zn(1)-N(1)	2.086(2) Å	C(6)-N(2)	1.475 (3) Å
Zn(1)-N(2)	2.145 (2) Å	N(2)-C(7)	1.472 (3) Å
Zn(1)-N(1A)	2.084 (2) Å	N(2)-C(7)	1.472 (3) Å
N(1)-If(1)	1.725 (2) Å	C(7)-C(8)	1.519 (3) Å
N(3)-If(2)	1.711 (2) Å	C(8)-N(3)	1.453 (3) Å
N(1)-C(5)	1.483 (3) Å		
N(1)-Zn(1)-N(2)	85.1(1) °	Si(1)-N(1)-Zn(1)	119.5 (1) (2) °
N(1)-Zn(1)-C(1)	129.2 (1) °	Si(1)-N(1)-Zn(1A)	120.8 (1) °
N(1)-Zn(1)-N(1A)	93.7 (1) °	Si(1)-N(1)-C(5)	112.7 (1) °
N(2)-Zn(1)-C(1)	112.1 (1) °	Zn(1)-N(1)-Zn(1A)	86.3 (1) °
N(2)-Zn(1)-N(1A)	109.4 (4) °	Zn(1)-N(1)-C(5)	106.2 (1) °
C(1)-Zn(1)-N(1A)	120.1 (1) °	Zn(1A)-N(1)-C(5)	108.0 (1) °

Fig. 1



CLAIMS

1. Compounds of general formula I



(1)

in which

M represents an element of group 12;

R_M represents the hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio, arylthio, amino, alkylamino, dialkylamino, cycloalkylamino, di(cycloalkyl)amino, alkyl(cycloalkyl)amino, arylamino, diarylamino, alkylarylamino or (cycloalkyl)arylamino radical;

A and B represent, independently, a carbon chain of 2 to 4 carbon atoms, optionally substituted by one or more of the following substituted or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, an alkyl, nitro or cyano radical;

L_1 and L_2 represent, independently, a group of formula $-E_{15}(R15)-$ in which

E_{15} is an element of group 15 and

R_{15} represents the hydrogen atom; one of the following substituted or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, an alkyl, nitro or cyano radical; a radical of formula $-E_{14}RR'R''$ in which E_{14} is an element of group 14 and R, R' and R" represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or arylthio radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; or a radical of formula $-SO_2Q$ in which Q represents a halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by

one or more substituents chosen from the alkyl, haloalkyl and halogen radicals;

L_3 indifferently represents a group of formula $-E'_{15}(R'_{15})(R''_{15})$ or $-E_{16}(R_{16})$ in which

E'_{15} is an element of group 15 and

E_{16} is an element of group 16 and

R'_{15}, R''_{15} and R_{16} represent, independently, the hydrogen atom; one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl or aryl radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; a radical of formula $-E'_{14}TT'T''$ in which E'_{14} is an element of group 14 and T, T' and T'' represent, independently, the hydrogen atom or one of the following substituted (by one or more identical or different substituents) or non-substituted alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, alkylthio, cycloalkylthio or arylthio radicals, in which said substituent is a halogen atom, the alkyl, nitro or cyano radical; or a radical of formula $-SO_2Q'$ in which Q' represents a halogen atom, an alkyl, haloalkyl or aryl radical optionally substituted by one or more substituents chosen from the alkyl, haloalkyl and halogen radicals.

2. Compounds of formula 1 as defined in claim 1, characterised in that they are presented in the form of a monomer or a dimer.

3. Compounds of general formula 1 as defined in one of claims 1 to 2, characterised in that

R_M represents an alkyl group;

A and B represent, independently, a carbon chain of 2 to 4 carbon atoms;

L_1 and L_2 represent, independently, a radical of formula $-E_{15}(R_{15})-$ in which E_{15} is a nitrogen or phosphorus atom and R_{15} represents a hydrogen atom or a radical of formula $-E_{14}RR'R''$ in which E_{14} represents a carbon or silicon atom and R, R' and R'' represent, independently, the hydrogen atom or an alkyl radical;

L_3 represents a radical of formula $-E'_{15}(R'_{15})(R''_{15})$ in which E'_{15} is a nitrogen or phosphorus atom, and R'_{15} and R''_{15} represent, independently, a hydrogen atom or a radical of formula $-E'_{14}TT'T''$ in which E'_{14} represents a carbon or silicon atom and T, T' and T'' represent, independently, the hydrogen atom or an alkyl radical.

4. Compounds of general formula 1 as defined in one of claims 1 to 3, characterized in that M represents a zinc atom.

5. Compounds of general formula 1 as defined in one of claims 1 to 4, characterized in that

R_M represents a methyl radical;

A and B represent, independently, a carbon chain of 2 carbon atoms;

L_1 and L_2 represent, independently, a radical of formula $-E_{15}(R_{15})-$ in which E_{15} is a nitrogen atom and R_{15} represents a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula $-E_{14}RR'R''$ in which E_{14} represents a silicon atom and R, R' and R'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical;

L_3 represents a radical of formula $-E'_{15}(R'_{15})(R''_{15})$ in which E'_{15} is a nitrogen atom, and R'_{15} and R''_{15} represent, independently, a hydrogen atom, a methyl, ethyl, propyl, isopropyl radical or a radical of formula $-E'_{14}TT'T''$ in which E'_{14} represents a silicon atom and T, T' and T'' represent, independently, the hydrogen atom or a methyl, ethyl, propyl or isopropyl radical.

6. Compounds of general formula 1 as defined in one of claims 1 to 4 and corresponding to the following formulae:

- $[Me_3SiN(H)CH_2CH_2N(Me)CH_2CH_2NSiMe_3]ZnMe$;
- $[Me_3SiN(H)CH_2CH_2N(H)CH_2CH_2NSiMe_3]ZnMe$.

7. Compounds of formula 1 as defined in claim 6, characterised in that they are presented in dimer form.

8. Process for the preparation of the products of general formula 1 as defined in claim 1, characterized in that a product of formula I

$$(L_1\text{-}A\text{-}L_2\text{-}B\text{-}L_3)^-\ ,\ Y^+ \quad (I)$$

in which L_1, A, L_2, B and L_3 have the meanings indicated in claim 1 and Y represents the hydrogen atom, a metal or a metallic group, is reacted with a product of formula II

$$MR_MZ \quad (II)$$

in which M and R_M have the meanings indicated in claim 1 and Z represents a parting group, in order to obtain a product of formula 1.

9. Use of the products of formula 1 as defined in any one of claims 1 to 7, as polymerization or copolymerization catalyst.

10. Use according to claim 9 for the polymerization or copolymerization of heterocycles, in particular epoxides such as propylene oxide.

11. Use according to claim 9, for the polymerization or copolymerization of cyclic esters, in particular the polymer cyclic esters of lactic and/or glycolic acid.

12. Process for the preparation of block or random copolymers, or polymers which consist of bringing into contact with one or more monomers, a chain initiator and/or a regulator, a polymerization catalyst and optionally a polymerization solvent, at a temperature comprised between ambient temperature and 250° C, for a duration comprised between a few minutes and 300 hours, said process characterized in that the chain initiator and/or the regulator and the polymerization catalyst are represented by the same compound which is chosen from the compounds according to claims 1 to 7.

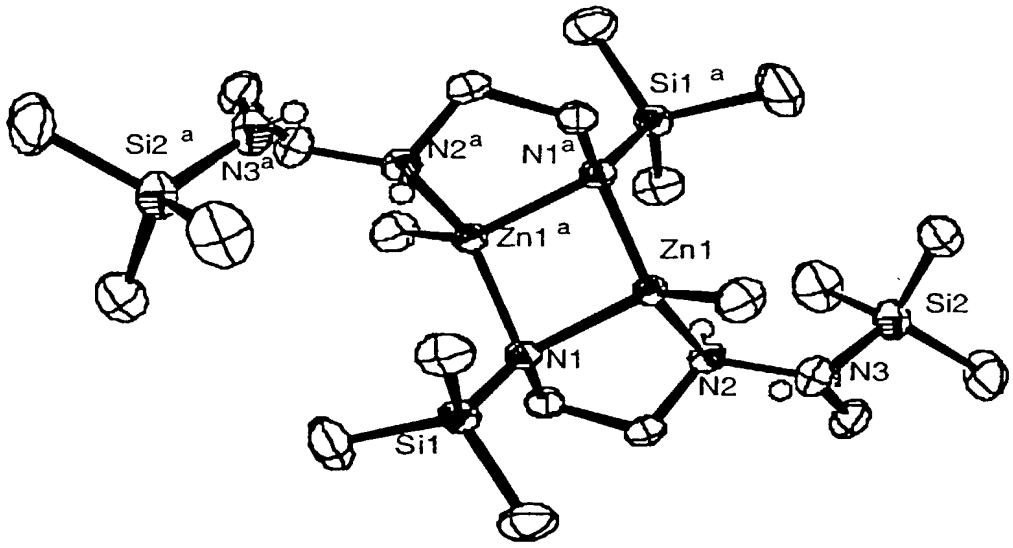
13. Process according to claim 12, characterized in that the monomer is chosen from the epoxides, and in particular propylene oxide, or the cyclic esters, and in particular the polymer cyclic esters of lactic and/or glycolic acid.

14. Polymers or copolymers which can be obtained by carrying out a process according to one of claims 12 or 13.

ABSTRACT

The present invention relates to new compounds having an element of group 12 and having a tridentate ligand, a process for their preparation and their use in particular as a polymerization catalyst.

Fig. 1



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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

[X] Declaration Submitted with Initial Filing OR [ ] Declaration Submitted after Initial Filing

Attorney Docket Number	
First Named Inventor	H. NGUYEN NGOC
COMPLETE IF KNOWN	
Application Number	
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled :

POLYMERISATION CATALYSTS

(Title of the invention)

the specification of which

[ ] is attached hereto

OR

[X] was filed on (MM/DD/YYYY) 06/23/2000 as United States Application Number or PCT International

Application Number PCT/FR00/01753 and was amended on (MM/DD/YYYY) _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	NO
99 401585.7	Europe	06/25/1999	[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]
			[ ]	[ ]	[ ]

[ ] Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	
		[ ] Additional provisional application numbers are listed on a supplemental priority sheet attached hereto

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Approved for use through 9/30/98. OMB 0651-0032
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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DECLARATION

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Name	Registration Number	Name	Registration Number
Charles A. Muserlian	19,683		
Jordan B. Bierman	18,629		
Donald C. Lucas	31,275		
Bierman, Muserlian and Lucas	18,818		

(4)

☐ Additional registered practitioner(s) named on a supplemental sheet attached hereto.

Direct all correspondence to:

Name	BIERMAN, MUSERLIAN & LUCAS				
Address					
Address	600 Third Avenue				
City	NEW YORK	State	New York	ZIP	10016
Country	U.S.A.	Telephone	(212) 661-8000	Fax	(212) 661-8002

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name	Hanh	Middle Initial		Family Name	NGUYEN NGOC	Suffix e.g. Jr.	
Inventor's Signature	[signature]					Date	November 22nd, 2001
Residence: City	THANH PHO HO CHIMINH	State		Country	VIETNAM VNX	Citizenship	Vietnamese
Post Office Address	Truong Dai Hoc Bach Khoa Tp hcm Khoa Cong Nghe Hoa Hoc						
Post Office Address	268 Ly Thuong Kiet, Q 10						
City	THANH PHO HO CHIMINH	State		Zip		Country	VIETNAM

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

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ADDITIONAL INVENTOR(S) Supplemental Sheet

2-00

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Middle Initial	Family Name	Suffix e.g. Jr.
Heinz		GORNITZKA	

Inventor's Signature: [signature] Date: Nov 8th 2001

Residence: City	State	Country	Citizenship
POMPERTUZAT IRL		FRANCE IRL	German

Post Office Address: 11 rue Les Balcons du Lauragais

Post Office Address:

City	State	Zip	Country
POMPERTUZAT		F-31450	FRANCE

3-00

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Middle Initial	Family Name	Suffix e.g. Jr.
Blanca		MARTIN-VACA	

Inventor's Signature: [signature] Date: November 8th 2001

Residence: City	State	Country	Citizenship
TOULOUSE IRL		FRANCE	Spanish

Post Office Address: 91 avenue d'Italie

Post Office Address:

City	State	Zip	Country
TOULOUSE		F-31400	FRANCE

4-00

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Middle Initial	Family Name	Suffix e.g. Jr.
Didier		BOURISSOU	

Inventor's Signature: [signature] Date: 12Nov. 2001

Residence: City	State	Country	Citizenship
PLAISANCE DU TOUCH IRL		FRANCE IRL	French

Post Office Address: 7B chemin de Charlas

Post Office Address:

City	State	Zip	Country
PLAISANCE DU TOUCH		F-31830	FRANCE

5-00

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Middle Initial	Family Name	Suffix e.g. Jr.
Guy		BERTRAND	

Inventor's Signature: [signature] Date: November 14, 200

Residence: City	State	Country	Citizenship
RIVERSIDE CA	CA	U.S.A.	French

Post Office Address: 5700 Lochmoor Drive

Post Office Address: Appt 144

City	State	Zip	Country
RIVERSIDE	CA	92507	U.S.A.

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

6-80

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ADDITIONAL INVENTOR(S) Supplemental Sheet

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Jean-Bernard	Middle Initial		Family Name	CAZAUX	Suffix e.g. Jr.	
Inventor's Signature	[signature]				Date	12.11.01	
Residence: City	ARAMON FRX	State		Country	FRANCE	Citizenship	French
Post Office Address	73 rue Emile Jamais						
Post Office Address							
City	ARAMON	State		Zip	F-30390	Country	FRANCE

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	

☐ Additional inventors are being named on supplemental sheet(s) attached hereto

(Janvier 1997)

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PRIORITY DATA (Supplemental Sheet)

Additional foreign applications:

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	NO
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
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			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐

Additional provisional applications:

Application Number	Filing Date (MM/DD/YYYY)

Additional U.S. applications:

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(if applicable)*

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REGISTERED PRACTITIONER INFORMATION (Supplemental Sheet)

Name	Registration Number	Name	Registration Number